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MONITORING AGENCY DOCUMENT NO: _____

ASTIA DOCUMENT NO: AD _____

CONTRACT AF 61(052)-46

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TECHNICAL REPORT

THERMOCHEMISTRY OF SELECTED
RADICAL RECOMBINATION REACTIONS

By

S. Sunner

Thermochemistry Laboratory,^{x)} University of Lund, Sweden

15 January 1962



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ABSTRACT: The photolysis of primary or secondary aliphatic disulfides in an organic matrix at 77°K quantitatively leads to the reaction

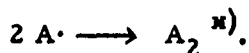
$$R'R''CHSSCHR'R'' \longrightarrow R'R''C=S + HSCR'R''.$$

Strong evidence is presented for the formation of stabilized thiyl radicals when a thiol is photolyzed. A few other compounds have been studied strengthening the view that two large radicals cannot simultaneously be formed and separately trapped in the system studied. Thus, one of the basic difficulties cannot be overcome in developing a method for the determination of radical recombination energies by warming up a solid solution of trapped, identical radicals, generated in situ. At least, this statement should be valid in dealing with simple not highly resonance-stabilized molecules.

INTRODUCTION

The determination of bond energies is one of the principal objects of molecular energetics. For covalent bonds it can be done in one or both of two principally different ways. Either, the direct determination of a specific fragmentation of a molecule may give a value of the bond dissociation energy of a particular bond, or, from thermochemical heat of combustion or heat of reaction measurements a value of the thermochemical bond energy term may be derived¹.

It should be of considerable theoretical value to devise a method for the direct measurement of bond formation energies by studying calorimetrically the radical recombination reaction



Such a method was used by Bichowsky and Copeland^{2, 3(p. 26)} in determining the heat of formation of H_2 from hydrogen atoms. These were obtained by flowing H_2 through an electric discharge. From measurements of the change in pressure and of the heat release at a platinum surface, the recombination energy was obtained. Obviously, this method is limited to a few cases with very small molecules, where the dissociation process can be unambiguously established.

To achieve a more general applicability it was deemed necessary to turn to the study of the production and behaviour of radicals in a condensed state. The problems to be coped with here are connected with the fulfilment of the following conditions:

1. One - and only one - radical species must be generated in an otherwise non-reactive system.
2. The nature and the amount of the radical must be established.
3. During the procedure the system must be reasonably stable.
4. The recombination reaction must be clean.
5. Further, it must be initiated and completed within the boundaries of a calorimetric system.

x) For obvious reasons, this experiment can be performed unambiguously only if the two radicals are identical. In the case of ionic species or formation of bonds of an electron donor-acceptor type the species must of course be different.

Although it was realized that it would be a formidable task to find ways and means by which these conditions could be fulfilled and that the ultimate goal certainly was quite remote, it was felt that results which might be gained could easily justify a careful exploration of the possibilities inherent in this experimental approach.

EXPERIMENTAL APPROACH

The first and second conditions given above were judged to be the most crucial. Although in recent years a very pronounced interest has been shown in the study of free radicals and a considerable amount of information has been gained^{4,5}, still very little is known about stoichiometric relations in radical formation processes. This being so, the assumption was made that, provided means could be found to split homolytically a symmetrical molecule into two identical radicals, the chemistry of the overall process should be very much simplified. Among a number of possible classes of substances symmetrical aliphatic disulfides were chosen.

According to the results obtained by a number of investigators who have reported on the stability of many radicals trapped in a rigid matrix at 77°K, the fulfilment of the third condition should not present any difficulties^{6,7}. Provided condition 1 could be realized, it was judged that the fourth condition should be more or less automatically fulfilled.

The fifth condition puts severe restrictions on both the methods for formation as well as for determination of the concentration of reactant and reaction products. The calorimetric procedure required the size of the sample container to be at least a few milliliters and its shape to approach spherical symmetry. Thus, some of the most common techniques for radical formation as well as trapping were out of the question. It was therefore decided to start out by exploring the method used by Lewis and Lipkin⁶, Norman and Porter⁷ and others, namely, to photolyze a compound at liquid nitrogen temperature in a rigid matrix consisting of a mixture of organic solvents and - as a possible analytical tool - to study the spectral changes in the UV- and visible regions. To establish the amount and identity of stable reaction products gas-liquid chromatography (GLC) should be extensively used.

Thus, it was required to design and build a unit for photolysis as well as a compartment for work at liquid nitrogen temperature accomodating an appropriately designed sample cell and an identical reference cell to be used in connection with a recording double-beam spectrophotometer.

GLC-methods had to be worked out for the detection of small amounts of foreign substances both in the hydrocarbons used as glass-forming solvents as well as in the solutions containing disulfides and decomposition products therefrom.

In the course of the work it was found necessary to study the temperature dependance of viscosity and melting curves for the glass-forming hydrocarbon mixtures and methods had to be worked out for this purpose.

INSTRUMENTS AND METHODS

Photolysis and spectrophotometry

The photolysis set-up^S consisted of two high-pressure mercury lamps (Philips SP 900 W) mounted on each side of the cell compartment and equipped with appropriate cooling devices (pressurized air and water) and filters (nickel sulfate solution and cut-off glass filters). The total amount of irradiation passing the filter solution was measured and found to be 1.8×10^{17} quanta per second and cm^2 at the position of the sample cell.

The sample cells and cell compartment^S. The cylindrical sample cells were made of quartz with sealed-on optically polished Ultrasil windows having an outside diameter of 22 mm and an inside diameter of 19 mm. The cells were each 17 mm in length. The use of a double-beam spectrophotometer required the design and construction of a compartment accomodating two identical cells. In order to avoid the use of complicated quartz Dewar vessels a design originally devised by Nelson¹⁰ was further developed, in which expanded polystyrene was used as an insulating material.

Our cell compartment consisted of two metal cans with an inner can made of stainless steel, accomodating the sample cell and the reference cell, and an outer can made of aluminum. The space between the cans was filled with foamed-in-place polyurethane. Evacuated quartz cylinders, allowing light to pass freely through the quartz cells, were mounted in the walls of the cell compartment. The inner can served as a container for liquid nitrogen and the cells were completely surrounded by the coolant. The fact that the optical path had to pass two 1 mm layers of liquid nitrogen has never caused any trouble even though spectra have been systematically recorded down to 200 mμ. It is relevant, however, that the nitrogen used was of 99.8 % purity or better and that it had to pass a quartz-wool filter just before it was blown into the compartment.

The storage capacity of the compartment was such as to allow three to three and a half hours of continuous undisturbed work on one filling of liquid nitrogen.

Spectrophotometry. A Unicam model SP 700 double-beam recording spectrophotometer was used with the low-temperature cell compartment substituted for the standard one.

Performance. Once the instruments and methods of operation had been developed, very few difficulties were encountered. The photolysis unit has worked very well with one exception - the aluminum coating on the surface of the reflectors for the mercury lamps quickly deteriorates and has to be replaced from time to time. The cell compartment has been used in over 400 runs. A couple of times a quartz cylinder broke and the replacement was time-consuming until the construction was changed. The choice of foamed-in-place plastics was found to be crucial. Of the few types tested only one was found to work satisfactorily (Nopco Lockfoam E-302). The most common difficulty encountered with the other types tested was that the plastic foam cracked during cooling causing an increased heat leakage.

The reproducibility of the spectrophotometric results between completely different runs (solutions prepared at different times) was at 298°K better than 0.05 kc. cm⁻¹ in wave-numbers and 1% in transmission and at 77°K 0.05 kc. cm⁻¹ in wave-numbers and 2% in transmission. The use of a double-beam spectrophotometer for photolysis studies seems therefore to be well justified.

Matrices and methods for matrix studies.

It was found of interest to try to develop a matrix from hydrocarbons without tertiary carbon atoms. This was done and a mixture of n-pentane and neo-hexane was found to be suitable¹¹.

To obtain knowledge of the matrices used a number of properties were studied separately¹². In order to correct properly for the change in concentration when going from room temperature to 77°K, the contraction was measured for the different matrices.

The literature gives very qualitative statements about the fluidity of a glass at 77°K. It was therefore decided quantitatively to measure the relative viscosity of the different matrices as a function of temperature in order to find the critical temperature region at which glasses start to become fluid. A very simple falling-body technique was developed.

Melting curves were studied to gain information on possible phase transitions in the glass. A simple technique was devised for this purpose using the thermometric method. In order to achieve a constant dissipation of energy over a wide temperature interval, a special method was developed¹³ (Cf Ref. 14).

Differential calorimetry.

A prototype of a twin-system was built in which it should be possible to perform the photolysis and the spectrophotometry within the boundaries of a calorimetric system. The work with this prototype was discontinued when it was found that all efforts must be directed towards the study of the basic conditions of the experimental approach.

RESULTS

Alifatic disulfides and mercaptans.

It has been conclusively proven that the photolysis of an alifatic disulfide in a rigid organic matrix does not lead to the formation of thiyl radicals¹⁵. Instead, the following reaction occurs quantitatively - within the precision of the analytical

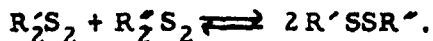
technique used:



in which $R_1 = \text{Alk}$, $R_2 = \text{Alk, H}$.

The proof is based on the following facts:

1 a. The photolysis of a mixture of symmetrical disulfides at room temperature led to a rapid disproportionation according to:



The equilibrium between pairs of disulfides ($R' = \text{Et}$, $R'' = \text{Me}$, $i\text{-Pr}$, $t\text{-Bu}$) was studied separately¹⁶.

1 b. At 77°K no detectable disproportionation occurred, indicating that diffusion of large molecules or molecular fragments is completely or almost completely hindered in the matrix.

2 a. When primary or secondary disulfides were photolyzed, the change in spectrum was very regular and the existence of a sharp isosbestic point indicated that the chemical reaction behind the spectral change was very simple.

2 b. The spectral change followed very closely a first-order rate equation.

2 c. Contrary to this, the spectral change following the photolysis of $t\text{-Bu}_2S_2$ was complex and did not allow a simple analysis. An elucidation of the chemistry in this case was not attempted.

3. The formation of the thiol RSH, corresponding to the disulfide R_2S_2 , was demonstrated by GLC, the amount of thiol formed followed a first-order rate equation.

4. During photolysis an absorption maximum developed at the wave-number where $C=S$ absorbs light. Upon standing at room temperature this absorption peak slowly decreased and at the same time an increase in absorption occurred in a region where the cyclic trimer to the thio aldehyde or thioketone absorbs light. The position of the isosbestic point observed agreed within the limits of error with that calculated from the known absorption curves for the monomeric and trimeric thioaldehydes.

5 a. When a thiol was photolyzed a well-defined absorption maximum developed¹⁷. Strong evidence was accumulated for the belief that this peak was due to the presence of thiyl radicals. The reaction is analogous to those investigated by Porter et al.^{7,8}. Appreciable amounts of disulfide were isolated after warm-up from the photolyzed thiol glasses.

5 b. When disulfides were photolyzed, no trace was found of the thiyl radical absorption peak.

Miscellaneous compounds.

A few exploratory experiments were performed on diphenyl disulfide and hydrazobenzene. The diphenyl disulfide photolyzed in the matrix at 77°K and three prominent spectral features were noted: 1) an absorption peak developed at about the same wave-number as that of the peak found when alkane thiols were photolyzed, 2) a peak which is attributed to benzenethiol and 3) a band structure which was not accounted for (Cf. Ref. 6). Upon photolysis the hydrazobenzene gave rise to the spectrum of azobenzene.

Partly to check the methods used, and partly to study the diffusion of iodine atoms, a few iodine-containing substances were photolyzed¹⁹. The observation, of Sowden and Davidson²⁰, that I₂ does not photolyze in a rigid matrix was confirmed. It was further found that the photolysis of HI and EtI gave rise to identical unstable intermediates and that HI₂ did not seem to be involved. The spectrum of a molecular compound between HI and I₂, most probably HI₃, was recorded in separate experiments. The observation of Norman and Porter⁷ was confirmed - namely that the viscosity of the matrix plays an important role in the photolysis of EtI.

CONCLUSIONS

From the results it is apparent that a homolytic splitting of an alifatic disulfide into two identical radicals cannot be accomplished in situ in a rigid matrix. All experimental evidence indicates that the statement should be true whenever the radicals to be produced are fairly large in size. The separation of the two fragments from each other is completely or almost completely hindered by the surrounding matrix molecules - an illustration to the importance of the cage-effect. If larger radicals have to be trapped, it must be done by deposition i. a. from the gaseous state. In this case, however, it seems to be very difficult to devise a calorimetric method capable of giving results of a sufficiently high precision.

The research has clearly demonstrated a new way of studying intramolecular rearrangements or interrational reactions under controlled conditions: the reacting molecule is trapped and is thus unable to interfere with or to be attacked by individual, identical molecules. It seems that the properties of, for example, simple alifatic thioaldehydes or thioketones can be very well studied by this technique, although they cannot be obtained in a pure state (with the exception of a few complicated structures).

FUTURE RESEARCH PLANS

The work initiated by this Contract will end with this Report. The research program will, however, continue and be further directed towards the study of

1. the thiyl radical and its properties,
2. controlled reactions of a photoexcited molecular species,
3. controlled reactions between photolytically produced radicals and the surrounding matrix molecules and
4. the fate of a split-off hydrogen atom or alkyl radical,

The ultimate goal will be to elucidate the detailed chemistry following a single well-defined photoexcitational process. A more extensive knowledge of the stoichiometry of radical reactions and of the conditions under which the radical reactions proceed might easily solve at least part of the problem - that is, how to determine radical recombination-reactions calorimetrically.

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